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Mobile Air Conditioner Refrigerant Evaluation

Acurex Corp., Research Triangle Park, NC

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16. ABSTRACT The paper discusses an evaluation of refrigerant from mobile air conditioners. The data gathered indicate that CFC-12 refrigerant does not degrade significantly with use. Furthermore, while small amounts of contaminant are removed with the refrigerant during servicing, most of the contaminants remain with the compressor oil. Current servicing practices do not require that the compressor oil be changed unless the compressor is replaced. The presence of HCFC-22 in concentrations above the specification for new CFC-12 (0.5%) is rare; it occurred in less than 1% of the 227 cars tested. HCFC-22 contaminant quickly leaks out of the automotive air conditioner through hoses and does not appear to cause operational problems while in the system.

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INTRODUCTION

Approximately 25 percent of domestically consumed chlorofluorocarbons (CFCs) are currently used in automobile air conditioners—the single largest use of these chemicals. Moreover, current servicing practices result in substantial but unnecessary emissions of CFC-12 (dichlorodifluoromethane). During typical servicing: first, any CFC-12 remaining in the automobile air conditioner is vented to the atmosphere; then, a new charge of CFC-12 is sometimes used to test the system and locate leakage; and finally, the system is recharged with CFC-12 after repair.

In an effort to reduce the amount of CFC compounds released, automobile manufacturers, servicing trade associations, and recycling equipment manufacturers worked together to develop a standard for recycled CFC-12 for automobile air conditioners. Some equipment for draining, cleaning, storing, and returning refrigerant to the system during servicing is presently available, and many companies are working to introduce improved designs. The recovery/recycling equipment currently available is sometimes used during the servicing of fleet vehicles such as buses that hold large refrigerant charges, but it is rarely used to reclaim the refrigerant during automobile servicing.

It was assumed that the release of CFCs to the atmosphere could be reduced by recovery and reuse of the refrigerant from automobile air conditioners when they are serviced; however, little information was available on the level of contamination in operating automobile air conditioners and the ability of equipment to satisfactorily clean the CFC for reuse.

As a result, a project to evaluate CFC refrigerant contamination from automobile air conditioners was carried out[1]. The quality of refrigerant present in vehicles of different makes, ages, and mileages and from different parts of the U. S. was assessed. The refrigerant from 227 vehicles with both failed and properly working air conditioners was collected and tested. The results of the program have provided an understanding not only of the quality of the refrigerant found in automobiles but also of how failure of the compressors and other equipment affects contamination.

The work was guided by and performed in cooperation with an ad hoc industry group representing:

- Environmental Protection Agency (EPA)
- Mobile Air Conditioning Society (MACS)
- Motor Vehicle Manufacturers Association of the United States (MVMA)
- Manufacturers of small recovery/reclamation/recycle devices
- American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE)
- Small air conditioning shops
- Underwriters Laboratories
- Other industry representatives and individuals

The ad hoc group agreed that the recycled CFC would not have to meet specifications for virgin CFC. They agreed that a standard of purity comparable to that of CFC-12 in automobiles that have been in use for 15,000 miles* (plus or minus 3,000 miles) with properly working air conditioners would be adequate. The group decided to work cooperatively to define the acceptable standard of purity and to simultaneously work toward development and certification of recycling equipment to satisfy this standard.

The first step in the program was to decide on the parameters that needed to be measured to determine the quality of the refrigerant. The ad hoc industry group agreed that the following parameters would fully describe possible refrigerant contaminants:

1. Moisture content
2. Acidity
3. High boiling residue
4. Purity of gas phase
5. Purity of liquid phase
6. Chloride ion

*Readers more familiar with metric units are asked to use the conversion factors at the end of this paper.

The two main objectives of the program were: (1) to determine the purity of the refrigerant using the six parameters listed above for properly working air conditioners in cars that had been driven 15,000 plus or minus 3000 miles, and (2) to determine the maximum refrigerant contamination for cars that will seek service due to major component failure. In response to these objectives, refrigerant in a population of vehicles from different parts of the U. S. with a variety of mileages and automobile air conditioners was evaluated. The program had the following main components:

1. Determine the level of impurity found in refrigerant of vehicles presently on the road at varying mileages with properly functioning and defective automobile air conditioning systems.

2. Determine whether the degree of degradation (if any) is the same for each region of the U. S. or whether variabilities such as climate and level of use result in a variation in the quality of the refrigerant.

EXPERIMENTAL PROGRAM

The protocol for this sampling and analysis program called for a statistically significant sample both from cars with properly functioning air conditioners and from those in the service center specifically for a problem with the air conditioner. The goal was to select cars at service centers around the country with the following mileages and/or malfunction:

1. 15,000 plus or minus 3000 (12,000 to 18,000) miles

2. 40,000 to 60,000 miles

3. 90,000 and greater miles

4. Cars of any mileage with defective compressors or other components that would likely cause overheating and result in deterioration of the refrigerant.

Efforts were also made to select a percentage of cars that represents the share of the U. S. market from the four categories of manufacturers listed below:

1. General Motors

2. Ford Motor Company

3. Chrysler Corporation

4. Foreign manufacturers

Because the sampling program was limited by availability of vehicles while sampling personnel were at the automobile repair shops, it proved difficult in spite of many attempts to do so to select cars of different manufacture and restricted mileage ranges in the numbers specified. It was decided, therefore, to relax these constraints and sample cars in the desired mileage ranges and not be as restrictive on the category of manufacturer as called for in the sampling plan. A good mix of cars from the four categories of manufacture was achieved in this way. A subsequent statistical evaluation of the data indicated that the objectives of the study were met under this less restrictive sampling plan.

To determine whether climate and use were factors in refrigerant deterioration, samples were taken from service centers in the following four areas:

1. Texas-Louisiana area (Gulf Coast): hot and humid to hot and arid weather; mostly long-distance driving

2. Maryland (Mid-Atlantic): hot and humid weather; mostly short-distance, heavy-traffic driving

3. Northern Ohio (Midwest): hot and humid part of year and very cold weather

4. Denver, Colorado (Mountain): low humidity weather; high altitude

The sampling program was performed in three stages. The first was a preliminary program to test the sampling procedure and estimate the level of variability that was likely to be encountered in the subsequent program. This preliminary estimate of the level of variability was necessary to determine the number of samples that needed to be taken for a statistically valid sample size. For this stage, 12 cars in the Research Triangle Park, North Carolina, area were sampled.

The second stage called for approximately 120 cars to be sampled at service centers in the Gulf Coast area. For the third stage, approximately 40 cars were to be sampled at a single air conditioning service center in each of three other geographical areas. Table I shows the actual number of cars sampled in each geographical area. As can be seen, the goal of 120 from the Gulf Coast area was not achieved because of the limited number of cars available from any one site during the sampling program.

Table I. Number of cars sampled

Geographic area	Number cars sampled
Gulf Coast	107
Northeast	40
Midwest	40
Mountain	40
Total	227

The sampling equipment used, shown in Figure 1, consists of the following components:

1. Sampling container

2. Sampling line

3. Manifold gauge set and vacuum pump

Three hundred sampling containers that were manufactured specifically for this purpose were used for this program. Each container is an (approximately) 1-gal. steel vessel equipped with a 2-way valve suitable for CFC-12.

The sampling line, which is shown in Figure 1 as the line within the broken rectangle and which is made of 1/4-in. flexible copper tubing, was used only once to prevent the risk of cross-sample contamination. One line was made up for each sample container and shipped with it. Prior to shipment, these lines were flushed with CFC-113, blown out with nitrogen, and capped.

The manifold gauge set and vacuum pump along with the ancillary tubing are standard equipment at all automobile air conditioning repair shops and were provided by the service centers where the sampling took place. Since no refrigerant flows through these lines, no special effort was necessary to ensure their cleanliness. Nevertheless, after the sampling equipment was hooked up but before sampling was started, a small amount of refrigerant was vented through the manifold gauge set to purge the lines.

At the sampling site, the sampling containers were filled with refrigerant from the automobiles by placing the sample container in a pan of dry ice and evacuating the line and container. The sample was then drawn from the air conditioner from the high pressure side so that lubricant would be withdrawn with the refrigerant. Once the sampling was completed, the air conditioning system was serviced if needed and then recharged by service personnel following normal procedures.

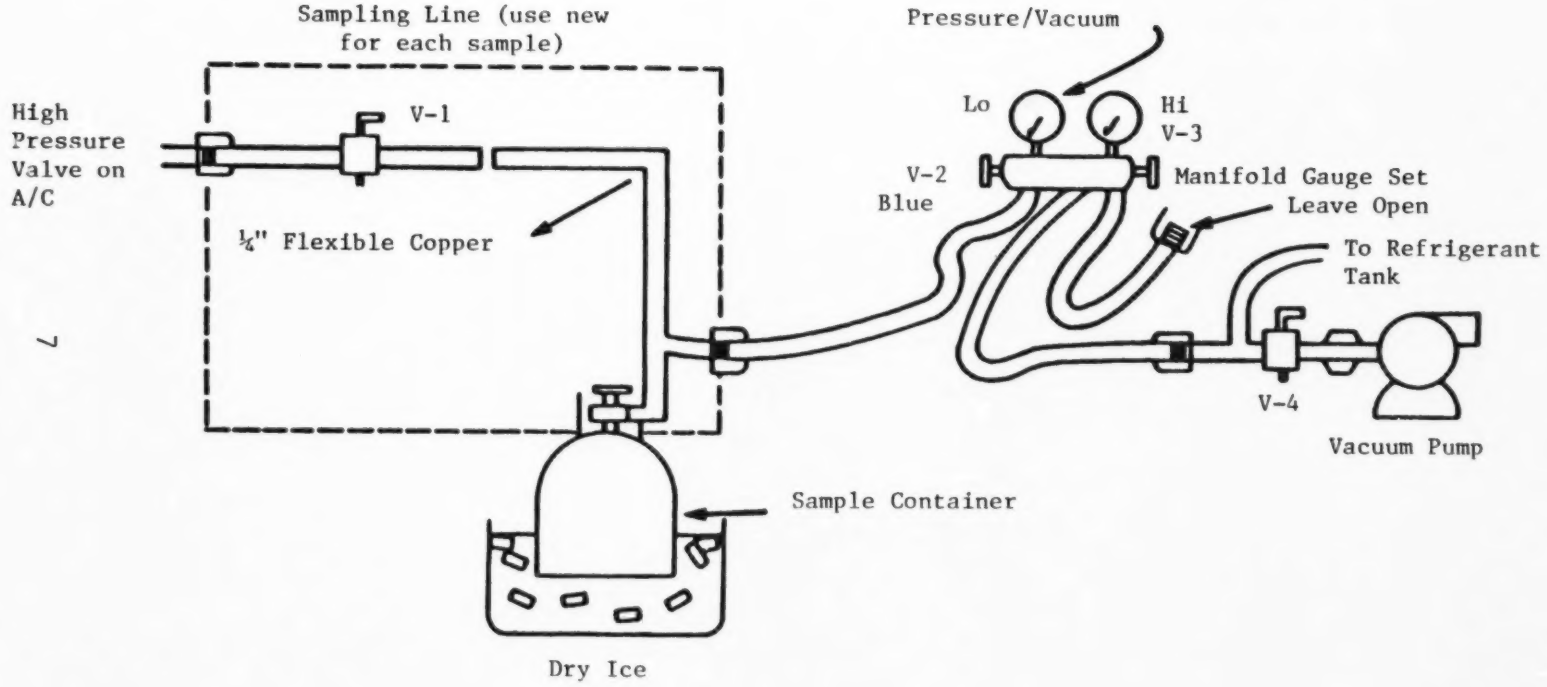

Figure 1. Sampling schematic

ANALYTICAL PROCEDURES

All samples were shipped to EPA's Air and Energy Engineering Research Laboratory in Research Triangle Park, North Carolina, for testing by Acurex Corporation, an on-site contractor. The contents of each sample container were analyzed as received by the method[2,3,4,5,6,7] indicated for the following:

1. Moisture content: Karl Fischer titration

2. Acidity or acid number: KOH titration

3. High boiling residue or oil content: Gravimetric analysis

4. Cleanliness or purity of the refrigerant: Determined by gas chromatography

5. Purity of the residue: Determined by gas chromatography

6. Free halides: Ion chromatography

The first three tests listed above are standard wet analyses commonly used throughout the industry. The moisture content test is a Karl Fischer (K-F) titration procedure, with only minor modifications. The acidity of the sample is determined by potassium hydroxide (KOH) titration, typically done to a bromothymol blue endpoint, although other indicators are sometimes used. The high-boiling residue or oil content of the refrigerant is typically measured by slowly evaporating the contents of a small weighed sample cylinder and rinsing the residue from the walls of the cylinder into a tared dish which is reweighed after the rinsing solvent is evaporated.

Two purity tests were conducted: one on the refrigerant gas phase and one on the residue. The gas phase purity was tested to determine whether the CFC-12 was contaminated with other refrigerants or volatile products of decomposition. It was hypothesized that this type of contamination could occur because of previous improper recharging or because the refrigerant had decomposed to a lighter material.

Both these measurements were made with a gas chromatograph equipped with a flame ionization detector (GC/FID). Attempts were made to identify the types of impurities found by the use of GC equipped with a mass spectrometer; however, the concentrations of impurities in all samples were too low to be identified.

The purity of the gas phase of the refrigerant was checked by injecting a sample into the GC with a gas sample loop. The purity of the residue was checked by evaporating a weighed quantity of liquid refrigerant from a pressure bomb, rinsing the interior of the bomb with solvent, and injecting the solvent into the GC/FID.

The test for inorganic chloride determined if the refrigerant had decomposed because of severe thermal stress. Because CFCs are exceptionally resistant to hydrolysis, chemical decomposition, especially under the mild conditions in an automobile air conditioner, is uncommon. Indeed, no free chlorides or fluorides were found. This test was performed by extracting the sample with a buffered aqueous solution and then analyzing the extract for chloride or fluoride ion. The standard analytical method for doing this is bubbling the refrigerant into silver nitrate solution. Free chlorides would show up as a precipitate. This method was felt to be far too insensitive to be used for this program. Rather, the buffered aqueous solution was analyzed using an ion chromatograph (IC), a procedure which is sensitive to approximately 500 parts per billion (ppb) of free chloride or fluoride.

RESULTS

The results of the analyses for acidity, chloride, fluoride, and refrigerant purity are given in Table II. None of these parameters (except for two refrigerant purity samples which are discussed below) exceeded the levels specified for new CFC-12. Neither the compressor oil nor the refrigerant showed any measurable level of acid over 1 ppm. The fact that no acid or inorganic chloride and fluoride was found in any of the samples was of initial concern. The analytical methods were checked using specially prepared samples of known concentrations of these analytes and were found to be sensitive to the following levels:

- Acid - 1 ppm as HCl
- Inorganic chloride - 500 ppb
- Inorganic fluoride - 500 ppb

Extensive testing of standards and duplicate samples showed a high level of reliability and reproducibility in the analytical method. A series of cocktails of propionic acid ($CH_3CH_2CO_2H$) were prepared at concentrations from 1 to 100 ppm. It was found that above approximately 5 ppm the analyses matched the expected value. Below this limit, the analyses correlated poorly with the actual concentrations of acid. Therefore, the laboratory technique accurately confirmed that acid in the CFC was less than 1 ppm and in the air conditioner less than 5 ppm.

Table II. Results of analyses: acids, halides, refrigerant purity

Analyte	Concentration	Analytical Method
Acidity	<5 ppm as HCl	Titration
Chloride ion	<0.5 ppm	IC
Fluoride ion	<0.9 ppm	IC
Refrigerant contaminant level[a]	<0.5%	GC/FID

[a] Two samples exceeded 0.5%. One contained 2% HCFC-22 and another contained 5% HCFC-22.

The chloride and fluoride ions typically form by hydrolysis of the CFC-12 producing hydrochloric or hydrofluoric acid. The lack of these ions, coupled with the high purity seen in the CFC-12 itself, indicates that refrigerant does not break down under the conditions encountered in an automobile air conditioner.

The refrigerant purity analyses also showed very little contamination. Only two samples of refrigerant out of 227 tested were found to contain more than 0.5 percent HCFC-22. Sample 262 measured 2 percent and Sample 218 measured 5 percent HCFC-22. The two cars were from the same location and had similar mileages (74,387 and 78,947, respectively). Sample 262 came from a 1973 model whose air conditioner had been recharged at approximately 60,000 miles. Sample 218 came from a 1977 vehicle. Both vehicles' air conditioners were performing to the satisfaction of the owners and were not being serviced at the time the samples were collected. The source of the HCFC-22 is uncertain. The most likely source is that, at some point in their service life, the air conditioners in both of these cars had been recharged with HCFC-22 by an inexperienced person.

The results of the analyses for moisture and residue purity are given in Table III.

The quantity of residue in each sample depended on the amount of refrigerant in the air conditioner, the rate at which the sample was removed (the sampling rate), and on the time between air conditioner use and sample removal. The quantities of residue ranged from 0 to 180,000 ppm with a mean of 15,000 ppm for all samples. The residue detected in the samples is primarily compressor oil which was carried over into the sampling container by the refrigerant. No significant impurity, other than oil which is desirable, was found in the CFC.

The residue was found to be very pure (>99 percent in all but one or two samples). The impurity was found to consist of very small amounts of a large number of different organic compounds. The concentration of any one compound was too low to allow identification. Attempts were made to correlate the

TABLE III. Summary of moisture and residue purity results (ppm)

	Moisture				Residue purity			
	No.	Maximum	Mean	SD	No.	Maximum	Mean	SD
Good compressors (miles)								
0-12,000	15	207	34	50	16	7,600	1,841	2,300
12,000-18,000	49	127	34	28	47	9,900	1,969	2,353
18,000-40,000	39	1,002	73	189	39	10,600	1,656	2,327
40,000-60,000	25	413	56	77	23	6,600	1,246	1,558
60,000-90,000	41	224	49	36	41	9,700	1,230	2,277
>90,000	23	755	94	147	22	4,700	785	1,232
Subtotal	192				188			
Failed Compressors	24	515	58	100	26	5,700	852	1,208
Total	216				214			
Blanks	21	65	15	16	20	2,100	313	504

residue purity with car mileage, with whether the compressor had failed or not, and with the part of the country where the sample was taken. No correlation was found with any of these three parameters.

The mean for all moisture samples was 56 ppm. No correlation was found between the water content of the refrigerant and the area of the U. S. where the sample was taken; however, a correlation was found between the odometer reading of the car and the water content. The mean moisture content for cars up to 18,000 miles was 34 ppm. Above this mileage, the mean moisture content of the refrigerant in the different mileage ranges remained in the 56 to 94 ppm range. No statistical difference was found between the water content of systems having failed and functioning compressors.

STANDARD OF PURITY

Using the results of the EPA mobile air conditioner sampling and testing program, the ad hoc industry group agreed on the following standard for recycled refrigerant:

15 ppm by weight of moisture

4000 ppm by weight of mineral oil based lubricant

0.15 g of noncondensable gas per pound of refrigerant

The noncondensables were not measured during the EPA test program but the group agreed that the above limit should be included in the standard. The standard for moisture and oil has been approved by the auto industry and the standard for noncondensables is now being reviewed.

In addition to the standard of purity for reclaimed or recycled mobile air conditioner refrigerant, the ad hoc group also has proposed the following functional description for reclamation equipment:

Refrigerant reclamation equipment shall:

1 a. Incorporate a desiccant package that must be replaced when saturated with moisture and whose acid capacity is at least 5 percent by weight of total system dry desiccant; or,

b. Refrigerant reclamation equipment shall incorporate an alternative acid scavenging device or material that is proven to provide equivalent or better removal of acid and equivalent reliability in service to that provided by 1a.

2. Alert the service technician, by refrigerant sight glass or other means, to the need to replace or regenerate the desiccant package when saturated with moisture.

3. Incorporate an in-line filter of 15 µm or less.

4. Alert the service technician or automatically vent the recovery tank to remove noncondensable gases when the tank pressure exceeds 10 psi (subject to experimental verification) above refrigerant saturation pressure. Said venting must occur prior to using the material for system charging. An automated mechanism or manual procedure must be provided to ensure proper venting of noncondensable gases.

5. Provide an accurate means to measure oil that is separated from the refrigerant in 1 oz or smaller graduations.

6. Be compatible with leak detector dye that may be present in the refrigerant.

7. Take recycled refrigerant for recharging from the liquid phase only.

This functional description has been submitted to MVMA for approval by the auto industry.

CONCLUSIONS

This sampling and analytical program showed that the refrigerant in operating air conditioners is very pure. Acids do not accumulate in the refrigerant. Any impurities that accumulate in the air conditioning system are concentrated in the compressor oil. They are dissolved by the liquid phase of the refrigerant but are not carried over into the gas phase. The gas phase proved to be free of contaminants and equivalent in purity (as measured by a GC/FID) to new CFC-12.

Water content was the only parameter which was highly dependant on vehicle mileage. It tended to be greater in vehicles with higher mileage. However, even refrigerant in new vehicles had a moisture level greater than the 10 ppm specification for new CFC-12. This may be due to the small amount of moisture that is present on all manufactured parts such as the compressor, expansion valve, and hoses and to the migration of moisture through hose material. As illustrated by the relatively small standard deviations shown in Table III, the moisture in the lower mileage ranges does not vary as much as it does in the higher mileage ranges.

This increase in moisture at the 18,000-mile level could indicate the start of deterioration of the drying agent in the air conditioner. As the drying agent is saturated, the moisture is at a higher concentration and the variability increases.

The moisture level in the refrigerant did not show any correlation with geographic location or vehicle make.

Contamination of the CFC-12 with HCFC-22 is not widespread. Only two cars out of 227 tested contained more than the limit for new CFC-12 of 0.5 percent maximum. Even if it occurs, its effect is limited since it quickly leaks out of the system through the hoses and has a very limited effect on the air conditioner's performance.

Using results of the sampling and testing program, the ad hoc industry group proposed to the automobile industry a voluntary standard of 15 ppm moisture, 4000 ppm lubricant, and 0.15 g of noncondensable gas per pound of refrigerant for recycled automobile air conditioner refrigerant.

In summary, the data gathered here indicate that the CFC-12 refrigerant does not degrade significantly with use. Furthermore, while small amounts of contaminant are removed with the refrigerant during servicing, the bulk of the contaminants remain with the compressor oil. Current servicing practices do not require that the compressor oil be changed unless the compressor is replaced. The presence of HCFC-22 in concentrations above the specification for new CFC-12 is rare; it occurred in less than 1 percent of the cars tested. HCFC-22 contaminant quickly leaks out of the automotive air conditioner through hoses and does not appear to cause operational problems while in the system.

REFERENCES

1. Evaluation of Refrigerant from Mobile Air Conditioners, U. S. Environmental Protection Agency, EPA-600/2-89-009, (NTIS PB89-169882), February 1989.

2. ASTM D-3401-85: "Standard Test Method for Water in Halogenated Organic Solvents and Their Admixtures." May 31, 1985.

3. ASTM 2989-86 (reapproved 1981): "Standard Test Method for Acidity Alkalinity of Halogenated Organic Solvents and Their Admixtures." April 25, 1986.

4. Allied Chemical Company. Approved Procedure GP-GEN-2A: "Determination of Acidity in Fluorocarbons." 1983.

5. DuPont Method F3200.037.01 CW(P): "Determination of Boiling Range, Residue, Particulates." October 8, 1985.

6. ASTM Standard E700-79: "Water in Gases Using Karl Fischer Reagent." September 28, 1979.

7. ASTM Standard D-1533-86: "Waste in Insulating Liquid (Karl Fischer Reaction Method)." January 31, 1986.